I. ACTION OF THE GRIGNARD REAGENT ON STERICALLY HINDERED ESTERS
II. TRIMERIZATION OF DURYL VINYL KETONE

BY

EDMOND MILTON BOTTORFF

A.B., Hanover College, 1937

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE SCHOOL OF THE UNIVERSITY
OF ILLINOIS, 1941

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PART I.

ACTION OF THE GRIGNARD REAGENT ON STERICALLY HINDERED ESTERS

INTRODUCTION

The reaction between alkyl sulfates or sulfonates and the Grignard reagent has been used for alkylation. When methyl sulfate is employed, for example, the overall reaction is

$$2(CH_3)_2SO_4 + RMgX \rightarrow RCH_3 + CH_3X + (CH_3OSO_2O)_2Mg.$$

There is no point of unsaturation in sulfonic esters, and organomagnesium halides cannot add. If addition to the carbonyl group in esters of carboxylic acids could be prevented, it might be possible for such esters to serve as alkylating agents. Steric hindrance is known to reduce the rate of carbonyl addition reactions and seemed to offer a possible device for testing the suggestion. The present investigation was, accordingly, undertaken with the purpose of studying the reaction between organomagnesium halides and esters of highly hindered acids.

EXPERIMENTAL AND DISCUSSION OF RESULTS

The esters chosen for this work were alkyl esters of mesitoic acid, which were prepared by treating mesitoyl chloride with the appropriate alcohol. These esters would react with the Grignard reagent in boiling n-butyl ether solution to produce mesitoic acid and the alkyl halide derived from the alkyl group of the ester and the halogen of the Grignard reagent. No alkylation products could be found in any of the reactions. Benzyl mesitoate and phenylmagnesium bromide gave a tar instead of diphenylmethane.

Aryl mesitoates when treated with phenylmagnesium bromide yield p-dimesitoylbenzene.[1] This reaction was extended to the aryl esters of 2,4,6-triisopropylbenzoic acid. p-Tolyl 2,4,6-triisopropylbenzoate and phenylmagnesium bromide gave a small yield of p-di-(2,4,6-triisopropylbenzoyl)-benzene. Other aryl Grignard reagents gave no isolable products. Methyl- and ethylmagnesium halides yielded 2,4,6-triisopropylacetophenone and propionyl-2,4,6-triisopropylbenzene, respectively.

SUMMARY

Alkyl mesitoates suffer cleavage of the O-R bond when treated with organomagnesium halides. No alkylation products could be found.

p-Tolyl 2,4,6-triisopropylbenzoate yielded p-di-(2,4,6-triisopropylbenzoyl)-benzene when treated with phenylmagnesium bromide. Other aryl Grignards were without action on this ester.

PART II.

TRIMERIZATION OF DURYL VINYL KETONE

INTRODUCTION

The formation of cyclic compounds by the condensation of unsaturated compounds is of very general occurrence.[2] The tendency of olefinic and acetylenic compounds to polymerize, frequently leads to the formation of alicyclic derivatives. The yields of such cyclic compounds are often low, owing to the formation of linear polymers.

In order to study the effect of steric hindrance on the polymerization of vinyl ketones, Fuson and McKeever [3] have prepared and polymerized mesityl vinyl ketone. The chief product was a trimer which was shown to be 1,3,5-trimesitoylcyclohexane. The present investigation was undertaken to extend this reaction to duryl vinyl ketone.

EXPERIMENTAL AND DISCUSSION OF RESULTS

Duryl vinyl ketone was synthesized from β-chloropropionyl chloride and durene by the Friedel-Crafts method. Polymerization was induced by heating the ketone with anhydrous potassium carbonate in methanol solution. The chief product was a trimer, 1,3,5-triduryloylcyclohexane. Two isomers were isolated. An independent synthesis produced the higher melting form. Interconversion of these two isomers could not be effected by ultraviolet light.

SUMMARY

Duryl vinyl ketone has been made and polymerized. The chief product was a trimer, 1,3,5-triduryloylcyclohexane.

BIBLIOGRAPHY

[1] Speck, unpublished.

[2] Diels and Alder, Ann., 460, 98 (1928).

[3] Fuson and McKeever, J. Am. Chem. Soc., 62, 2088 (1940).

VITA

The writer was born in Milroy, Indiana, on September 14, 1916. He attended the public schools of Columbus, Indiana, and in 1933 matriculated at Hanover College. He was granted the degree of Bachelor of Arts in 1937, and in the fall of the same year he entered the graduate school of the University of Illinois. He held a teaching assistantship in inorganic chemistry from 1937 to 1940 and a University fellowship during 1940-1941.

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